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<p>(54) Title: POLYKETONE SOLUTIONS (57) Abstract A polymer solution comprising a polyketone polymer dissolved in a liquid comprising a dissolved salt which salt is selected from the alkali and alkaline earth metal salts; a method of preparing the polymer solution, a method of recovering the polyketone from the solution; and a process for preparing a filament fibre or film.</p>		

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## POLYKETONE SOLUTIONS

This invention relates to solutions of alternating aliphatic polyketone polymers, a method for preparing the solutions, a method for recovering the polyketone polymers from the solutions and a process for preparing a filament fibre or film from the solutions.

Polymers of carbon monoxide and ethylenically unsaturated compounds commonly referred to simply as aliphatic polyketones have been known for some time. Alternating aliphatic polyketones (hereafter, "polyketones" or "polyketone polymers") are of considerable interest because they exhibit a good overall set of physical and chemical properties. This class of polymers is disclosed in numerous US patents, exemplified by US-A-4880903 and US-A-4880904, which are incorporated herein by reference. These polymers have a breadth of useful properties giving them established utility as premium thermoplastics in the production of shaped articles such as gears, bearings, pipes, hose, connectors, fibre and parts for the automotive industry. The polymers display high strength, toughness, rigidity, dimensional stability, hydrolytic stability and resistance to abrasive wear among other favourable properties which they retain under a wide range of conditions such as temperature, the presence of moisture, and the presence of harsh chemical agents. For example, thinly moulded parts comprised of polyketones have shown excellent property retention in concentrated acidic solutions.

A process for preparing fibres by solution spinning of polyketones is described in US-A-5045258, which is incorporated herein by reference. This process employs hexafluoroisopropanol (HFIPA), m-cresol, and mixtures

thereof as solvents for the polyketones. Solvents such as these present handling difficulties among other problems. US-A-5194210 proposes solution spinning of polyketone fibres. The patent proposes that mixtures of organic compounds can be used to dissolve the polymer for use in the process. The mixture includes solvents such as ethylene carbonate or propylene carbonate and an aromatic alcohol free of alkyl radical substituents such as resorcinol, phenol, and hydroquinone.

It has now been found that preparations based on a dissolved alkali and alkaline earth metal salt can dissolve polyketones completely, even at room temperature. These preparations can be used as solvents for producing filament fibre or film of polyketones. This considerably expands the range of methods for preparing such objects.

The present invention relates to a polymer solution comprising a polyketone polymer dissolved in a liquid comprising a dissolved salt which salt is selected from the group of the alkali and alkaline earth metal salts, on the understanding that if the liquid consists of  $\text{ZnCl}_2$  dissolved in water the concentration of  $\text{ZnCl}_2$  is less than 62 %w, based on the total weight of  $\text{ZnCl}_2$  and water.

A second aspect of the invention relates to a method of preparing a polymer solution which method comprises dissolving a polyketone polymer in a liquid comprising a dissolved salt which salt is selected from the group of the alkali and alkaline earth metal salts, on the understanding that if the liquid consists of  $\text{ZnCl}_2$  dissolved in water the concentration of  $\text{ZnCl}_2$  is less than 62 %w, based on the total weight of  $\text{ZnCl}_2$  and water.

A third aspect of the invention relates to a method of recovering a polyketone from a solution of a polyketone polymer in a liquid comprising a salt dissolved in a liquid medium which salt is selected from

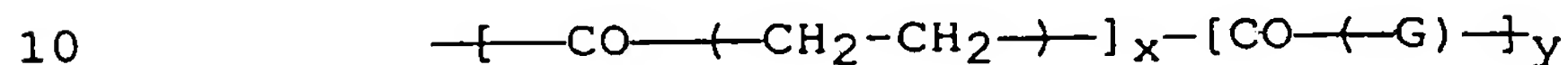
the group of the alkali and alkaline earth metal salts, which method of recovering comprises the step of reducing the salt concentration of the solution or cooling down the solution, and recovering the polyketone polymer.

5 A fourth aspect of the invention relates to a process for preparing a filament fibre or film by passing a solution of a polyketone polymer in a liquid comprising a dissolved salt which salt is selected from the group of the alkali and alkaline earth metal salts, through the  
10 orifice of a die to spin a filament in the form of a film or a fibre, coagulating the filament and removing liquid from the coagulated filament. After the removal of liquid the filament may or may not be drawn.

The polyketones for use in this invention are  
15 alternating copolymers of carbon monoxide and at least one olefinically unsaturated compound. The alternating structure implies that the polymers contain one molecule of carbon monoxide for each molecule of the olefinically unsaturated compound. Olefinically unsaturated compounds  
20 comprise suitably up to 20 carbon atoms and include compounds which comprise exclusively carbon and hydrogen and compounds which in addition comprise hetero atoms, such as unsaturated esters, ethers and amides. Unsaturated hydrocarbons are preferred. Examples of  
25 suitable olefinically unsaturated compounds are aliphatic  $\alpha$ -olefins, such as ethene, propene, butene-1 and hexene-1, cyclic olefins such as cyclopentene, aromatic compounds, such as styrene and  $\alpha$ -methylstyrene and vinyl esters, such as vinyl acetate and vinyl propionate. The  
30 preferred polyketone polymers are alternating polymers of carbon monoxide and ethene or alternating polymers of carbon monoxide, ethene and an olefinically unsaturated compound of at least 3 carbon atoms, particularly an  $\alpha$ -olefin such as propene.

35 When the preferred polyketone polymers of carbon monoxide, ethene and another olefinically unsaturated

compound are employed, there will be within the polymer typically at least 2 units incorporating a moiety of ethene for each unit incorporating a moiety of the other olefinically unsaturated compound(s). Preferably, there will be from 10 units to 100 units incorporating a moiety of ethene for each unit incorporating a moiety of the other olefinically unsaturated compound(s). The preferred polyketone polymers are therefore represented by the repeating formula



where G is the moiety of the olefinically unsaturated compound of at least 3 carbon atoms polymerized through the ethylenic unsaturation and the ratio of y:x is typically no more than 0.5, more typically from 0.01 to 0.1. When alternating polymers of carbon monoxide and ethene only are employed, there will be no second olefinically unsaturated compound present and the polymers are represented by the above formula wherein y is zero. When y is other than zero the  $\text{---CO---}(\text{CH}_2\text{---CH}_2\text{---})$  units and the  $\text{---CO---}(\text{G})\text{---}$  units are found randomly throughout the polymer chain. The precise nature of the end groups does not appear to influence the properties of the polymer to any considerable extent so that the polymers are fairly represented by the formula for the polymer chains as depicted above.

The polyketone polymers of number average molecular weight from 1000 to 200,000, particularly those of number average molecular weight from 20,000 to 90,000 as determined by gel permeation chromatography are of particular interest. The polyketone polymers are in general linear polymers. Typical melting points for the polymers are from 175 °C to 300 °C, more typically from 210 °C to 270 °C, as determined by differential scanning



calorimetry. The polymers have typically a limiting viscosity number (LVN), measured in m-cresol at 60 °C in a standard capillary viscosity measuring device, from 0.5 dl/g to 10 dl/g, more typically from 0.8 dl/g to 4 dl/g.

Preferred methods for the production of the polyketone polymers are known from US-A-4808699 and US-A-4868282. US-A-4808699 teaches the production of polyketone polymers by contacting ethene and carbon monoxide in the presence of a catalyst comprising a Group VIII metal compound, an anion of a non-hydrohalogenic acid with a pKa less than 6 and a bidentate phosphorus, arsenic or antimony ligand. US-A-4868282 teaches the production of polyketone polymers by contacting carbon monoxide and ethene in the presence of one or more hydrocarbons having an olefinically unsaturated group with a similar catalyst.

The backbone chemistry of aliphatic polyketones precludes chain scission by hydrolysis. As a result, they generally exhibit long term maintenance of their property set in a wide variety of aqueous environments. This is in contrast to a material such as nylon 6,6 which suffers the consequences of hydrolysis. It has indeed been found that the solution of this invention is stable, which means that there is no significant change to the molecular structure of the polyketone. The polyketone solution comprises polyketone, indentifiable as such, in liquid state.

Many alkali and alkaline earth metal salts can be used in this invention. Preference is given to inorganic alkali and alkaline earth metal salts, i.e. salts which do not comprise entities which have a carbon atom and a hydrogen atom which are mutually linked by a covalent bound. Suitable salts are alkali and alkaline earth metal halogenides and thiocyanates. The alkali and alkaline earth metal salts are preferably selected from

lithium and zinc based salts. They are in particular selected from the group of salts of the general formulae  $ZnX_2$  and  $LiY$ , wherein X is selected from the group consisting of Cl, Br and I, and Y is selected from the group consisting of Br, I and SCN. LiBr and LiI are preferred lithium based salts.  $ZnCl_2$  is a preferred zinc-based salt.

The polymer solutions can be prepared by dissolving the polyketone in a liquid which comprises a dissolved alkali or alkaline earth metal salt. Suitable conditions for dissolving the polyketone relate to the salt concentration, the liquid medium in which the salt is dissolved, the temperature, and the quantity of polyketone which is desired to be dissolved.

The liquid medium is typically a polar medium, more typically a protic polar medium, in particular an aqueous medium. The liquid medium is typically water and/or a polar organic medium. The organic liquid medium is in particular an organic compound which has from 1-5 carbon atoms in its molecules. Organic compounds are understood to be compounds which have in their molecules a carbon atom and a hydrogen atom which are mutually linked by a covalent bond. Water is the most preferred liquid medium. Alcohols such as methanol and ethanol are the most preferred polar organic liquid medium. Other polar organic media are ketones, amides, esters, lactams, lactones, and the like.

The concentration of polyketone in the polymer solution is typically at least 0.1 %wt, preferably at least 0.5 %wt and it is typically less than about 25 %wt (based upon total weight of polyketone and liquid).

The temperature at which the polyketone is dissolved may vary within wide limits. Suitably the polyketone is dissolved at a temperature in the range of from -10 to



+180 °C. Preferably a temperature is selected in the range of from 20 to 140 °C.

The concentration of the salt dissolved in the liquid may vary between wide limits. Suitable concentrations are generally above 40 %wt, preferably above 45 %wt, based on the total weight of the salt and the medium in which the salt is dissolved. The upper limit of the salt concentration is generally determined by the limit of the solubility of the salt under the prevailing conditions. For practical reasons an upper limit of 80 %wt may be employed.

Generally speaking, there is a relationship between the salt concentration and the temperature at which the polyketone can suitably be dissolved. The skilled person will be able to identify suitable dissolution conditions by simple experimentation and the following examples may serve as guidance.

When the liquid is a solution of LiBr or LiI in water, the salt concentration is suitably selected greater than 56 %wt (based on total weight of water and salt) for dissolving the polyketone at 60 °C. As one increases the dissolution temperature, the salt concentration can be lowered. Thus, at 95 °C one may use a salt concentration of greater than 53 %wt LiBr (based on total weight of water and salt), to dissolve the same quantity of polymer.

Likewise, when the liquid is a solution of ZnCl<sub>2</sub> in water, the salt concentration is suitably selected greater than 61 %wt (based on total weight of water and salt) dissolving the polyketone at 23 °C. As one increases the temperature, the salt concentration can be lowered. Thus, at 95 °C one may use a salt concentration of greater than 56 %wt ZnCl<sub>2</sub> (based on total weight of water and salt), to dissolve the same quantity of polymer.

When the liquid is a solution of  $\text{ZnBr}_2$  in water, the salt concentration is suitably greater than 70 %wt (based on total weight of water and salt) at 60 °C. When the liquid is a solution of  $\text{ZnI}_2$ , the salt concentration is

5 suitably greater than 59 %wt (based on total weight of water and salt) at 60 °C.

For practical purposes, a linear relationship between the salt concentration and the temperature of dissolution can generally be interpolated between these

10 concentrations and temperatures, and can be extrapolated, e.g. to the practical limits of solubility of the salts.

The solutions of this invention are prepared by dissolving polyketone in a liquid comprising dissolved salt, as defined hereinbefore. Some addition of mixing

15 power is helpful but this merely accelerates dissolution and does not cause it. No special methods or techniques are necessary. Solutions so formed are generally stable and they may be stored in any type of vessel which does not permit osmosis, reaction, leaching, or evaporation of

20 solvent solution.

Polyketone can be readily precipitated or otherwise removed from the polymer solution by reducing the salt concentration of the liquid. For example, polyketone may already at least partly be removed from a solution of

25 polyketone in aqueous  $\text{LiBr}$  or  $\text{LiI}$  by reducing the  $\text{LiBr}$  or  $\text{LiI}$  concentration to less than 56 %wt at 60 °C. Generally speaking, it is preferred to reduce the salt concentration to a level below 45 %wt, in particular below 40 %wt. Reducing the salt concentration can be

30 done by adding to the solution -as a non-solvent- an additional portion of liquid medium (typically with less than 5 %wt salt dissolved therein, based on total weight of the liquid medium and the salt, preferably without any salt dissolved therein), for example by adding water

35 and/or organic polar medium. Reducing the salt concentration can also be done by precipitating salt (for

example, by the addition of a reagent such as  $\text{AgNO}_3$ ), or through other means of salt removal (e.g. by extraction, ion exchange or osmosis). The polyketone can also suitably be precipitated or otherwise removed by cooling the polyketone solution. The polyketone is suitably recovered as a solid or slurry. The polymer is then generally rinsed with a reagent such as water to further reduce the presence of residual salt.

The dissolution of polyketones is useful in removing polyketone from objects that are coated with polyketone. They may also be used to form polyketone films or coatings by preparing thin layers of a polyketone solution and then removing the polyketone from the liquid. Objects may be coated or encapsulated by contacting, as by dipping, the object into a solution of the polyketone solution, removing the excess solution, and then removing liquid.

Filament fibres or films can be spun by passing a polyketone solution in a liquid containing dissolved alkali or alkaline earth metal salt through the orifice of a die. The orifice of the die will typically be round, but can also be of other desired geometries. Dies having orifices of varied shape can be utilized to produce filaments having a wide variety of cross sectional designs, for example, round, square, rectangular, or elliptical. For instance, a die having a rectangular orifice can be utilised to produce a filament which is essentially in the form of a film. It is generally convenient to utilize a die having an orifice which is essentially circular. The orifice of such dies will typically have a diameter which is within the range of 30 to 400 microns. In most cases, it is preferred for such orifices to have a diameter which is within the range of 40 microns to 200 microns. A spinneret which is equipped with multiple holes can be used as the orifice, in order

to manufacture a multifilament fibre. Such holes may generally have a shape or diameter as specified above.

5 The polyketone solution is forced through the die at a rate which is sufficient to attain a spinning speed of 1 meter per minute to 1000 meters per minute. Typically, the spinning speed is between 2 meters per minute to 400 meters per minute. It is desirable to utilize the fastest possible spinning speed which does not result in unsatisfactory uniformity. Higher spinning speeds are also desirable because they result in higher throughputs and better productivity. For this reason, spinning speeds in excess of 1000 meters per minute would be desirable if uniformity and other desired properties can be maintained.

15 The polyketone solution is forced through the die utilizing an adequate pressure to attain the spinning speed desired. The polyketone solution will typically be solution spun into the solution spun filament at a temperature which is within the range of 20 °C to 180 °C. Higher or lower temperatures can be utilized but are not preferred.

25 It is preferred that most of the liquid is removed from the polyketone solution after passage through the die. This can be accomplished by passing the solution spun filament through a spinning bath containing liquid medium, as a non-solvent, such as water and/or the polar organic medium, as described and exemplified hereinbefore. This coagulates the polyketone filament. If drawing is applied, it is preferred to further remove liquid or remove non-solvent, prior to drawing. This minimizes the amount of chain relaxation which can occur and accordingly helps to maintain chain orientation.

30 The skilled person will appreciate that -although different terms have been used- there is no fundamental difference between "coagulation" and "precipitation" as referred to hereinbefore. In both cases the polyketone

polymer solution is contacted with a non-solvent which results in solidification of the polyketone.

The ability to utilize aqueous liquids with this invention provides considerable process advantages. In a preferred process of this invention, the filament is spun from a polyketone solution in an aqueous liquid containing the dissolved alkali or alkaline earth metal salt and it is coagulated by reducing the concentration of aqueous liquid therein such that the composition is outside the conditions suitable for dissolution of the polyketone at the given temperature. This can be done by passing the solution spun filament through a spinning bath containing an aqueous liquid as non-solvent, e.g. water, in the spinning bath described above. The polyketone is then recovered as a filament.

After the solution spun filament has been prepared and preferably after liquid removal, it may be subjected to a drawing procedure. During the drawing procedure the solution spun filament is drawn to a total draw ratio of at least 1:1 to 50:1. The total draw ratio will typically be within the range of 15:1 to 20:1. It is advantageous to utilize relatively high draw ratios to maximize the tensile strength and modulus of the polyketone filament being produced.

The drawing procedure can be carried out in a single drawing stage or preferably in multiple stages. Typical drawing temperatures are from 23 °C to 260 °C, preferably the drawing temperature is at least 10 °C below the melting point of the polyketone filament, as determined by differential scanning calorimetry. Additional drawing steps can also be utilized to attain the desired total draw ratio.

This invention is further described by the following non-limiting examples. The salt concentration in the liquids are specified in %wt of salt, relative to the

total weight of the liquid (i.e. the total weight of salt and water or methanol).

Example 1 (Polyketone Formation)

5 A terpolymer of carbon monoxide, ethylene, and propylene was produced in the presence of a catalyst composition formed from palladium acetate, the anion of trifluoroacetic acid and 1,3-bis(diphenylphosphino)-propane. The melting point of the linear terpolymer was 220 °C, as measured by differential scanning calorimetry, 10 and it had a limiting viscosity number (LVN) of 1.75 measured at 60 °C in m-cresol.

Example 2

Polymer produced according to Example 1 was injection moulded into ASTM D638, type V tensile bars, each 15 weighing 1.75 g. One tensile bar was immersed in 22 ml of a 65 %wt solution of LiBr in water and one tensile bar was immersed in 22 ml of a 60 %wt solution of LiI in water. The samples were maintained at 60 °C. The tensile bars dissolved completely.

20 Example 3

Example 2 was repeated except that the liquid was a concentrated solution of LiSCN in water. Complete dissolution occurred.

Example 4

25 A tensile bar prepared according to Example 2 was immersed in a 50 %wt solution of LiBr in methanol. The tensile bar almost completely dissolved at 23 °C after 456 hours.

Example 5 (Characterization)

30 Polymer produced according to Example 1 was injection moulded into ASTM D638, type V tensile bars, each weighing 1.75 g. A tensile bar was submerged in a glass jar containing about 50 ml of a 65 %wt solution of ZnCl<sub>2</sub> in water at about 60 °C for 120 hours. The polymer 35 dissolved completely. C<sup>13</sup> NMR analysis of the solution



revealed the presence of polyketone without any change in molecular structure of the polymer.

A 15 ml aliquot of the polymer solution was removed and the polymer recovered from it by the addition of 16 ml water followed by decantation. The precipitate was then washed with copious amounts of water and then the product was dried at 60 °C overnight in vacuum under nitrogen purge. The precipitate and a sample of the polymer from which it originated was then submitted to GPC analysis using HFIPA as a solvent and found to be nearly identical in molecular weight distribution. No generation of low molecular weight species were observed.

This example shows the stability of the polymer solutions produced according to this invention.

#### Example 6

Tensile bars described in Example 5 were prepared. One tensile bar was immersed in 50 ml of a 75 %wt solution of  $\text{ZnBr}_2$  in water at 60 °C. The tensile bar dissolved completely within 72 hours.

#### Example 7

Tensile bars described in Example 5 were prepared. One tensile bar was immersed in 50 ml of a 60 %wt solution of  $\text{ZnI}_2$  in water at 60 °C. The tensile bar dissolved completely in 312 hours.

#### Example 8

50 ml solutions of 65 %wt and 70 %wt  $\text{ZnCl}_2$  in water were prepared. A Type V tensile bar of the polyketone of Example 1 was added to each solution at 60 °C. Additional bars were added to each sample as dissolution occurred to determine the solubility limit of polyketone in the liquid. Viscous solutions were formed in each case. A maximum amount of 9.5% and 12.5% of polyketone polymer could be dissolved in these liquids respectively.

The example was repeated at 23 °C for the 65 %wt liquid only. Here a maximum of 7.5% polyketone polymer was soluble.

Example 9

5        A polyketone solution was formed as in Example 5.  
About 10 ml were drawn into a hypodermic syringe having  
an 18 gauge needle. The liquid was then ejected from the  
syringe and a polyketone filament was coagulated in a  
10       water bath by manually drawing the filament across the  
bath. The filament was then further rinsed with water.  
This produced filament which ranged in diameter from  
1.3 µm (0.05 mil) to 0.51 mm (20 mils). The filaments  
were then dried at about 60 °C in vacuum. The filaments  
were then manually postdrawn.

15       Example 10 (Prophetic)

Polyketone as described in Example 1 is dissolved in  
a 62 %wt solution of ZnCl<sub>2</sub> in water at 60 °C. The  
solution is stirred until a homogeneous polymer solution  
is obtained. The total polyketone concentration of the  
20       solution is about 7 %wt (based on weight of polymer and  
solvent). The polymer solution is spun through a  
spinneret having a capillary diameter of 250 microns into  
a spinning bath containing water to coagulate and produce  
a filament. The filament is then washed free of solvent,  
25       wound onto a spool, and dried. The filament is then  
drawn at 180°C and at draw ratio of 20:1. The filament  
fibre so produced has a tenacity of about 1.5 GPa, a  
modulus of about 20 GPa, and an elongation at break of  
about 7.5%.

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C L A I M S

1. A polymer solution comprising a polyketone polymer dissolved in a liquid comprising a dissolved salt which salt is selected from the group of the alkali and alkaline earth metal salts, on the understanding that if  
5 the liquid consists of  $\text{ZnCl}_2$  dissolved in water the concentration of  $\text{ZnCl}_2$  is less than 62 %w, based on the total weight of  $\text{ZnCl}_2$  and water.
2. A solution as claimed in claim 1, characterized in that the dissolved salt is selected from the group of  
10 salts of the general formulae  $\text{ZnX}_2$  and  $\text{LiY}$ , wherein X is selected from the group consisting of Cl, Br and I, and Y is selected from the group consisting of Br, I and SCN.
3. A solution as claimed in claim 2, characterized in that the dissolved salt is selected from the group  
15 consisting of  $\text{LiBr}$ ,  $\text{LiI}$  and  $\text{ZnCl}_2$ .
4. A solution as claimed in any of claims 1-3, characterized in that the medium in which the salt is dissolved is a protic polar medium, in particular an aqueous medium.
- 20 5. A solution as claimed in claim 4, characterized in that the medium is water.
6. A solution as claimed in any of claims 1-5, characterized in that the polyketone is an alternating polymer of carbon monoxide and an olefinically  
25 unsaturated compound which is selected from ethene and ethene and an olefinically unsaturated compound of at least 3 carbon atoms, in particular an  $\alpha$ -olefin.
7. A solution as claimed in any of claims 1-6, characterized in that the solution contains from  
30 0.5-25 %wt of the polyketone, based on the total weight of the polyketone and the liquid.

8. A method of preparing a polymer solution which method comprises dissolving a polyketone polymer in a liquid comprising a dissolved salt which salt is selected from the group of the alkali and alkaline earth metal salts, on the understanding that if the liquid consists of  $\text{ZnCl}_2$  dissolved in water the concentration of  $\text{ZnCl}_2$  is less than 62 %w, based on the total weight of  $\text{ZnCl}_2$  and water.

9. A method as claimed in claim 8, characterized in that the polymer is dissolved in the liquid at a temperature in the range of 20-140 °C.

10. A method of recovering a polyketone from a solution of a polyketone polymer in a liquid comprising a salt dissolved in a liquid medium which salt is selected from the group of the alkali and alkaline earth metal salts, which method of recovering comprises the step of reducing the salt concentration of the solution or cooling down the solution, and recovering the polyketone polymer.

11. A method as claimed in claim 10, characterized in that the salt concentration of the solution is reduced by adding liquid medium.

12. A process for preparing a filament fibre or film by passing a solution of a polyketone polymer in a liquid comprising a dissolved salt which salt is selected from the group of the alkali and alkaline earth metal salts, through the orifice of a die to spin a filament in the form of a film or a fibre, coagulating the filament and removing liquid from the coagulated filament.

13. A process as claimed in claim 12, characterized in that the filament is spun from a polyketone solution in an aqueous liquid containing the dissolved alkali or alkaline earth metal salt and it is coagulated by passing the solution spun filament through a spinning bath containing an aqueous liquid as non-solvent.

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14. A process as claimed in claim 13, characterized in that the spinning is carried out at a temperature within the range of 20 °C to 180 °C.

5 15. A process as claimed in claim 14, characterized in that after the removal of liquid the filament is drawn at a temperature from 23 °C to 260 °C and at least 10 °C below the melting point of the polyketone filament.